ELECTROCATALYSIS BY ALLOY ELECTRODES
I. OXIDATION OF FORMAMIDE*

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The electrochemical oxidation of formamide was studied in acid medium at platinized Pt, Pt–Pd, Pt–W, Pt–Ni and Pt–Au electrodes using galvanostatic method at steady state condition. The catalytic activity of Pt–Au alloy electrode, which was found to be better compared to other electrodes, was studied at different percentage compositions of gold. This alloy with 35 at. % gold showed maximum catalytic activity. The slope was found to be 120 mV per decade in the Tafel region and was constant for all the electrodes. The mechanism of the reaction was proposed by studying the system at different concentrations of formamide, and pH of the solution. The energy of activation for the reaction was calculated to be approximately 10 K. cal. mole^{-1}.

The work reported here was a part of the studies on the basic mechanisms of oxidation of organic compounds which can be used as fuels in fuel cells and the activities of the noble metal alloy electrodes in the oxidation process. In the present communication, the kinetics of the electrochemical oxidation of formamide at platinized Pt electrode in acid medium was studied and the comparison of the activity of the noble metal alloy electrodes Pt–Pd, Pt–W, Pt–Ni and Pt-Au was done. The optimum composition for maximum catalytic activity of Pt–Au alloy electrode, which was found to be better compared to the other electrodes, was determined.

Very little work has been reported on the anodic oxidation of formamide and other amides. Bagostski and coworkers[1] from their investigations of the anodic oxidation of formamide observed that the rate of oxidation of formamide at constant concentration (0.5 M) increases linearly when the pH is reduced from 11 to 0.5. William[2] fabricated a fuel cell taking monamides such as formamide, acetamide, and lauramide as fuels and conventional electrodes such as platinum black on nickel or nickel boride. These investigations[1,2], in which formamide was used as a fuel, made us to study the electrochemical characteristics of formamide, so that its application in fuel cell can be done in an effective way.

Experimental

The details of the set up and the experimental procedure for measuring the galvanostatic polarizations were mentioned elsewhere[3]. The test electrode and the auxiliary electrode were made of platinum foil of 2 cm^2 geometric area.

Platinum was deposited on platinum foil from a plating bath containing 1 gm of chloroplatinic acid dissolved in 50 ml of 2N hydrochloric acid with a current density of 10 mA cm^{-2} for 50 minutes. Depending on the compositions of the metals to be deposited, the bath was prepared by mixing salt solutions of the two metals in definite proportions. The electron microprobe analyser (MAR^2, USSR) was used to get the qualitative as well as quantitative data of the surface composition of the elements on the alloy electrodes.

The chloroplatinic acid, chloroauric acid, and palladium chloride were of Johnson Mathey & Co. Ltd. The remaining chemicals used were of BDH 'AnalaR' grade. Triply distilled conductivity water was used for preparing solutions. The sulphuric acid solution was preelectrolysed at a current density of 20 mA cm^{-2} for 24 hrs. in nitrogen atmosphere using platinized Pt electrodes to remove impurities. Formamide was purified according to the procedure given[4,5].

The electrode was activated just prior to use by electrochemical pulsing technique. Any trace of oxygen present in the test solution was removed by passing purified nitrogen gas. After stopping the flow of nitrogen gas the system was kept undisturbed to attain equilibrium, and then the current potential readings were taken at steady-state condition.

All the current density readings were reported on the basis of the geometric area and all the potentials were referred to normal hydrogen electrode (NHE). Temperature effects were studied using thermostat with an accuracy of ± 0.1°C. Unless otherwise specified all the readings were taken using 3N sulphuric acid at a temperature of 27°C.

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RESULTS AND DISCUSSION

(1) Kinetic Parameters

In the studies of electrochemical oxidation of formamide in acid medium platinized P', Pt-Pd, Pt-W, Pt-Ni and Pt-Au electrodes were used with 10 atomic % of added metal. From the current-potential curves for the above mentioned electrodes, as was shown in the Fig. (1), it can be observed that Pt-Au alloy

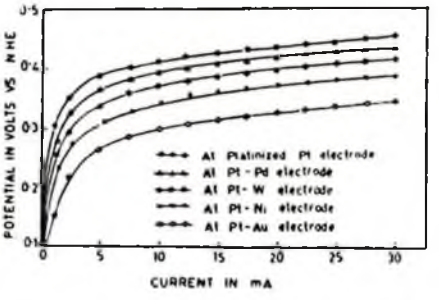


Figure (1) :

Current-potential diagram at different electrodes in 3N sulphuric acid and 1M formamide at 27°C.

electrode was a better electrocatalyst compared to any other electrode.

The catalytic activity of Pt–Au alloy electrode was found to change with the composition of the alloy (Figs. 2 and 3). Open circuit potential and rate of

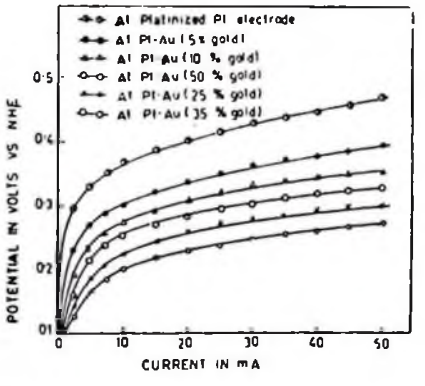
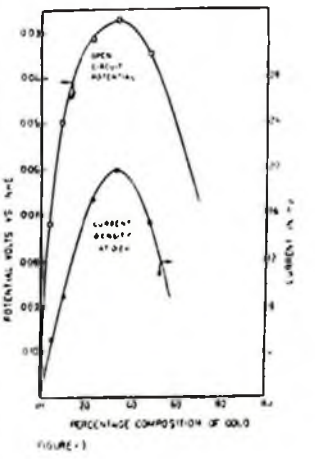


Figure (2) :

Current-potential diagram at Pt-Au alloy electrodes in 3N sulphuric acid and 1M formamide at 27°C.

oxidation were plotted against composition of gold in Pt–Au electrodes. Results indicated that the alloy electrode with 35 atomic % of Au will show maximum catalytic activity.



Percentage composition of gold vs open circuit potential and reaction rate in 3N sulphuric acid and 1M formamide at 27°C.

The surface composition of platinum and gold in the Pt–Au alloy electrodes were determined from the graphs obtained with the electron microprobe analyser. The quantitative estimation of the surface composition of Pt–Au alloy electrodes was done. Photographs obtained with the same instrument indicated that these two metals were distributed uniformly on the surface. Similar observations were made for the other alloy electrodes.

The Tafel slope for the above mentioned electrodes was found to be about 120 mV per decade in the lower potential region, as could be observed from the Fig. (4). At higher potentials, potential oscillations

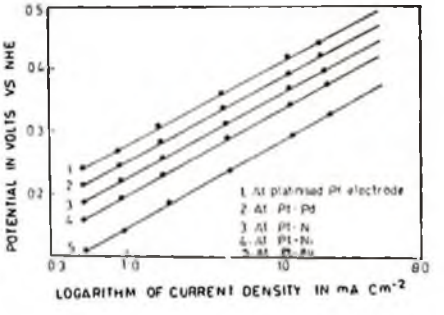


Figure (4) :

Logarithm of current density vs over voltage at different electrodes in 3N sulphuric acid and 1M formamide at 27°C.

were observed. This might be due to the fact that at higher potential (above 0.8 V vs NHE) formation of

oxide layer on the surface of the electrode material takes place and the electrochemical oxidation of formic acid might be inhibited by the oxide layer formed on the metal, thereby limiting the Tafel region. The Tafel slope was found to be independent of the concentration of formamide, pH of the solution and temperature of the system. The order of the reaction with respect to formamide below 1.0M was unity. Above this concentration, the rate was independent of the concentration of formamide. The order of reaction with respect to pH of the solution was found to be –1 upto the pH range studied (0.1 to 6.0). The order of reaction with respect to ammonium ion was found to be –1.

Increase of temperature decreased the polarization upto approximately 70°C but as the temperature was increased to higher values, the polarization was found to increase as was shown in the Fig. (5). The energy

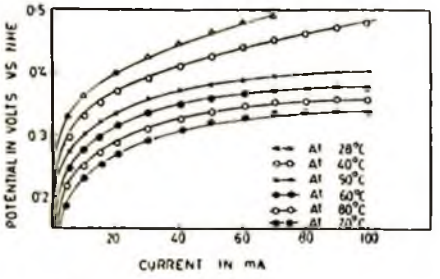


FIGURE-5

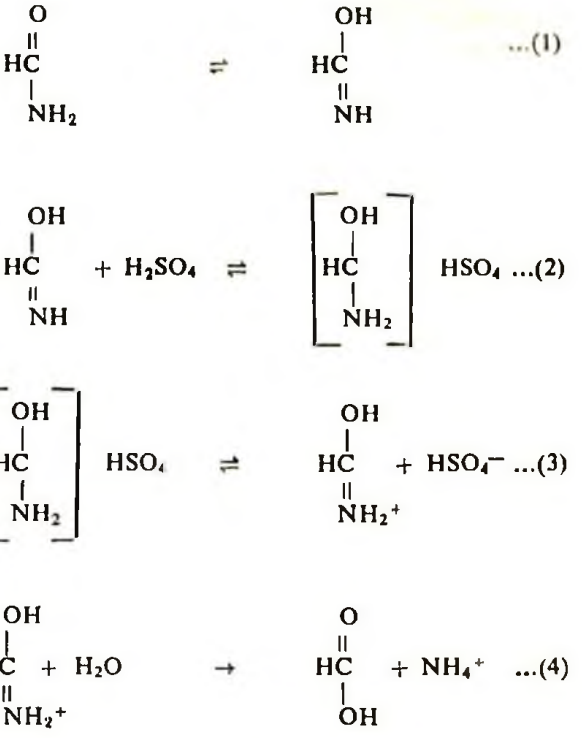
Current potential diagram of 1M formamide in 3N sulphuric acid on platinized Pt electrode at different temperatures.

of activation was found from the slope of the plot of log current density and inverse temperature, to be 10 K. cal mole^{-1} at open circuit potential in the temperature region starting from 25°C to 70°C. The anomalous behaviour at higher temperatures may be due to the difference in mechanism of the reaction through different adsorbed species[6] or by increased catalytic decomposition.

The gaseous oxidation product of formamide was collected by flushing with purified nitrogen gas, at room temperature. It was then analysed by an Orsat's apparatus, and was found to contain carbondioxide only.

(2) Reaction Mechanism

It was known that formamide undergoes acid catalysed hydrolysis forming formic acid and ammonium in according to the following reactions[7].



At the time of electrochemical oxidation, the system contains formamide, formic acid ammonium sulphate in sulphuric acid. Out of these, formic acid undergoes electro-oxidation. The effect of ammonium ion on the hydrolysis can be observed by the addition of ammonium sulphate along with formamide to sulphuric acid, as was shown in the Fig. (6), the order

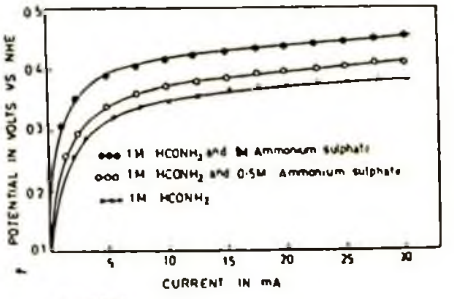


FIGURE-6

Current-potential diagram of formamide, formamide and ammonium sulphate in 3N sulphuric acid on platinized Pt electrode at 27°C.

of reaction with respect to ammonium ion being –1. This indicates that the salt decreases the hydrolysis.

A survey of mechanism studies on the electrochemical oxidation of formic acid indicates that a process involving the dissociative chemisorption of formic acid is favoured, based mainly on the work of Frumkin and co-workers [8,9] and Bagotskii et al [10], formic acid being adsorbed on to the electrode surface according to Langmuir type of isotherm.

According to the recent studies of Parsons and co-workers [11,12] and Adzic et al [13] the oxidation of formic acid on platinum most probably begins with oxidative dehydrogenation.

$$HCOOH \rightleftharpoons HCOOH_{ad} \quad ...(5)$$

$$HCOOH_{ad} \rightarrow COOH + H^+ + e \quad ...(6)$$

the main oxidation process being

$$COOH \rightarrow CO_2 + H^+ + e \quad ...(7)$$

The Tafel slope of 12 0 mV per decade indicates that the first electron transfer is the rate determining step. Now considering that, steps prior to rate determining step are in equilibrium, the reaction sequence can be written as :

$$HCOHNH_2 + H_3O^+ \rightleftharpoons [Complex] \quad ...(8)$$

$$[Complex] \rightleftharpoons HCOOH + NH^+_4 \quad ...(9)$$

$$HCOOH \rightleftharpoons HCOOH_{ad} \quad ...(5)$$

$$HCOOH_{ad} \rightarrow HCOO_{ad} + H^+ + e \quad ...(6)$$

$$HCOO_{ad} \rightarrow CO_2 + H^+ + e \quad ...(7)$$

Taking into consideration that step (7) as the rate determining step and assuming Langmuir type of adsorption, the rate expression can be written as

$$v = k\,(1-\theta_{org})\,{}^{c}HCONH_2\;\; {}^{c}H^{+}\;\; {}^{c-1}NH^{+}_4 \exp\left[\frac{\beta VE}{RT}\right] \quad ...(10)$$

where θ_{org} is the fractional coverage by the adsorbed organic, the remaining terms having their usual significance.

It was known that at potentials higher than 0 8 V, the formation of oxide layer begins on the electrode, which can be written as :

$$Pt + (H_2O)_n \rightarrow Pt\,(OH)_n + nH^+ + ne \quad ...(11)$$

$$Pt\,(OH)n \rightarrow Pt\,O_n + nH^+ + ne \quad ..(12)$$

This oxide layer inhibits the electrochemical oxidation of formic acid whic occurs through adsorption. This makes an increase in the Tafel slope.

(3) Electrocatalytic Activity

The electrocatalytic activities of the platinized platinum, platinum-palladium, platinum-tungsten, platinum-nickel and platinum-gold electrodes for the oxidation of formamide in acid medium at 27°C can be seen from the Fig. (1). From this figure it can be observed that all the alloy electrode systems are better than platinized platinum. Similar type of increase in the electrocatalytic activity of platinum by alloying it with Pd, Ni and Au were observed in the electrochemical oxidation of methanol in alkaline medium, formic acid in acid medium and hydrazine in acid medium[14].

The electrocatalytic activities of Pt-Au system at different, compositions were studied by Breiter[15] in the electrochemical oxidation of methanol in acid medium. He rules out the possibility that the d-band character effects the activity. According to the d-band vacancy, the d-band of Pt is gradually filled with the increasing gold content and filling up of the d-band is achieved between 30 and 40% gold for homogeneous alloys. Watanabe and Motoo[16] in their electrochemical oxidation of methanol in acid medium and alkaline medium at Pt – Au system observed an increase in the electrocatalytic activity of Pt by the addition of gold in alkaline medium. But in acid medium there was a continuous fall of activity by the addition of gold to platinum. According to the bi-functional theory of catalysis proposed by them, the electrocatalytic activity for the oxidation of an organic substance is enhanced by the co-operation of two kinds of metal atoms being mixed on the atomic scale and having different adsorption properties, one for organic species, one for oxygen containing species on the electrode surface in the negative potential range. Since gold has been ascertained to adsorb no organic species[17] and to adsorb oxygen containing species in alkaline solution at more negative potential than in acid solution, it can enhance the electrocatalytic activity of Pt only in the alkaline medium. The electrochemical oxidation of organic compounds through the oxide layer formed on the alloys, as was mentioned by Watanabe et al [18] does not seem to be possible, at least in the present case, as the electrochemical oxidation of formic acid is inhibited at higher potentials, where oxide layer formation on the alloys (about 0 75V vs NHE) takes place.

The increase in the electrocatalytic activity of Pt-Au alloys upto 35 a% gold even in acid medium, as was observed in the present investigation, which contradicts the previous observations, compared to platinized platinum, can only be explained on the basis of an increase in th active surface area This can be observed from the Fig. (2) of the previous communication[14], in

which the charging curves for the different electrodes were shown. This increase in the active surface area might be due to increase in the roughness of the sur face. This explanation will be valid upto 35 a% gold, where the activity reaches maximum. Above this composition in the homogeneous alloy system, there will be a separation of phase, one consisting platinum rich and another gold rich. This phase separation above the said maximum composition decreases the surface area. This can be observed, as was shown in the Fig. (3), from the fall in the catalytic activity of the alloy.

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